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(71) Applicant: **NGK INSULATORS, LTD.**  
**2-56, Suda-cho, Mizuho-ku**  
**Nagoya City Aichi Pref.(JP)**

(72) Inventor: **Kawasaki, Shinji**  
**2-15 Takeda-Cho 2-chome, Mizuho-Ku**  
**Nagoya City, Aichi Pref.(JP)**  
Inventor: **Ito, Shigenori**  
**37-210, 2-1, Iwanaridai 6-Chome**  
**Kasugai City, Aichi Pref.(JP)**  
Inventor: **Okumura, Kiyoshi**  
**205, Town Kameshiro, 2, Kameshiro-Cho**  
**2-Chome**  
**Mizuho-Ku, Nagoya City, Aichi Pref.(JP)**  
Inventor: **Yoshioka, Katsuki**  
**43, Takeda-Kita-Shataku, 9, Takeda-cho**  
**3-chome**  
**Mizuho-ku, Nagoya City, Aichi Pref.(JP)**

(74) Representative: **Paget, Hugh Charles Edward**  
**et al**  
**MEWBURN ELLIS 2 Cursitor Street**  
**London EC4A 1BQ(GB)**

(54) **Method for manufacturing solid oxide film and method for manufacturing solid oxide fuel cell using the solid oxide film.**

(57) A first method for manufacturing a solid oxide film having a highly densified solid oxide film having a small thickness and an improved electric conductivity; and a second method for manufacturing a solid oxide fuel cell in which a solid oxide film formed on an air electrode or a fuel electrode is manufactured by the first method. The solid oxide fuel cell according to the present invention is capable of generating a high power.

The solid oxide film is formed on a substrate in such manner that a solid oxide material is sprayed on the substrate to form a sprayed solid oxide film thereon; then a solution of metal compound including at least one metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc is impregnated into the sprayed solid oxide film; then the sprayed solid oxide film is subjected to a heat treatment in order to make an airtightness of the film high. It is possible to use a material for spraying, in which 1 ~ 10 parts by weight of an oxide of said metal is contained, instead of the impregnation, or to obtain a material for spraying by mixing the compound powder containing said metal and the solid oxide material in a spray gun via separately arranged powder supply devices.

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The present invention relates to a method for manufacturing solid oxide film and a method for manufacturing solid oxide fuel cell using the solid oxide film.

Recently, fuel cells have been noted as a power generating source. The fuel cell is capable of directly converting chemical energy possessed by fuel to electric energy. Since the fuel cell is free from the limitation of Carnot's cycle, the fuel cell essentially has a high energy conversion efficiency. Further, various fuels such as naphtha, natural gas, methanol, coal reformed gas and heavy oil may be used, additionally, these fuels may be used with a low pollutant level. Moreover, the power generating efficiency of fuel cells is not influenced by the scale of the equipment. Therefore, the power generation with the aid of fuel cells is an extremely promising technique.

Particularly, since the solid oxide fuel cell (hereinafter abbreviated as SOFC) operates at a high temperature of 1000°C or more, the reaction of electrodes thereof is very active and the use of a noble metal catalyst such as expensive platinum is not required. In addition, since the SOFC has a low polarization and a relatively high output voltage, the energy conversion efficiency is considerably higher than that of other fuel cells. Furthermore, since the SOFC is constructed with solid materials, it is stable in structure and has long life use.

In such SOFC, it is desired to make the solid oxide film thin as far as possible. However, in a chemical vapor deposition method or an electrochemical vapor deposition method, which are conventional methods for manufacturing the solid oxide thin film, there are drawbacks that an apparatus for manufacturing the solid oxide film becomes large, an area on which the solid oxide film can be formed is small and a processing speed for forming the film is late. Therefore, the cost for manufacturing the film becomes high and it is difficult to obtain a large solid oxide film. Additionally, in case of the electrochemical vapor deposition method, the shape of the substrate is limited to be cylindrical.

For instance, it has been known; ref. Sunshine Journal 1981, Vol. 2, No. 1 how to manufacture the solid oxide fuel cell with the aid of plasma spray coating; and the plasma spray coating is excellent in that a thin solid oxide film with a high density can be formed quickly in an easy manner.

Further, in Japanese Preliminary Patent Publication Nos. 61-198569 and 61-195570, it is known that it a spray substance, in which ceric oxide or zirconium oxide and metal oxide such as alkaline-earth metals or rare-earth element are soluted, is sprayed on a substrate with the aid of the plasma spray coating after the particle size of the material is adjusted it forms a solid oxide film on the substrate.

However, airtightness of the film formed by the plasma spray coating is generally low. Therefore, when a solid oxide film of the solid oxide fuel cell is formed by the plasma spray coating, the airtightness of the film is not sufficient. Therefore, when operating such SOFC, hydrogen, mono carbonate oxide, etc. is leaked through the solid oxide film. Then, the electromotive force per one SOFC becomes smaller than 1V, and the output thereof is decreased, so that the energy converting efficiency from fuel to electric power is aggravated.

In this case, it is considered to make the solid oxide film thick to prevent the leakage of fuel, however, a diffused resistor for an ion diffusion in a bulk becomes so large that a resistor of the cell becomes large. Therefore, it is strongly desired to develop a technique to improve the power output of the unit SOFC by making the solid oxide film thin and making the density of the film high unless the fuel leakage is not generated.

The present invention has for its first purpose to provide a method for manufacturing solid oxide film by which the solid oxide film can be formed with a thin thickness, a high density and an improved electric conductivity.

The present invention has for its second purpose to provide a method for manufacturing solid oxide fuel cell being applied the thin and highly densified solid oxide film thereto to obtain a solid oxide fuel cell having a high power output.

According to the first aspect of the present invention, a method for manufacturing a solid oxide film comprises the following steps:

preparing a solid oxide material;

spraying said solid oxide material on a substrate to form a sprayed solid oxide film;

impregnating a solution of a compound containing at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc into said sprayed solid oxide film; and

subjecting the solid oxide film to a heat treatment in order to improve airtightness of the solid oxide film formed on the substrate.

According to the second aspect of the present invention, a method for manufacturing a solid oxide fuel cell comprises the following steps of:

preparing a solid oxide material;

spraying said solid oxide material on an air electrode to form a sprayed solid oxide film on the air

electrode;

impregnating a solution of a compound containing at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc into said solid oxide film formed on the air electrode;

subjecting the sprayed solid oxide film to a heat treatment in order to improve airtightness of the solid  
5 oxide film; and

providing a fuel electrode film on a surface of the solid oxide film formed on the air electrode.

According to the third aspect of the present invention, a method for manufacturing a solid oxide fuel cell comprises the following steps of:

preparing a solid oxide material;

10 spraying said solid oxide material on a fuel electrode to form a sprayed solid oxide film on the fuel electrode;

impregnating a solution of a compound containing at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc into said solid oxide film formed on the fuel electrode;

subjecting the sprayed solid oxide film to a heat treatment in order to improve airtightness of the solid  
15 oxide film formed on the fuel electrode; and

providing an air electrode film on a surface of the solid oxide film formed on the fuel electrode.

According to the fourth aspect of the present invention, a method for manufacturing a solid oxide film comprises the following steps:

preparing a solid oxide material for spraying containing 1~10 parts by weight in total of an oxide of at  
20 least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc with respect to 100 parts by weight of solid oxide raw material;

spraying the thus prepared solid oxide material on a substrate to form a solid oxide film thereon;

subjecting the thus formed solid oxide film to a heat treatment in order to improve airtightness of the solid oxide film formed on the substrate.

25 According to the fifth aspect of the present invention, a method for manufacturing a solid oxide fuel cell comprises the following steps:

preparing a solid oxide material for spraying containing 1~10 parts by weight in total of an oxide of at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc with respect to 100 parts by weight of solid oxide raw material;

30 spraying the thus prepared solid oxide material on an air electrode to form a solid oxide film thereon;

subjecting the solid oxide film formed on the air electrode to a heat treatment in order to improve airtightness of the solid oxide film; and

providing a fuel electrode on a surface of the solid oxide film formed on the air electrode.

According to the sixth aspect of the present invention, a method for manufacturing a solid oxide fuel cell  
35 comprises the following steps:

preparing a solid oxide material for spraying containing 1~10 parts by weight in total of an oxide of at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc with respect to 100 parts by weight of solid oxide raw material;

spraying the thus prepared solid oxide material on a fuel electrode to form a solid oxide film thereon;

40 subjecting the solid oxide film formed on the fuel electrode to a heat treatment in order to improve airtightness of the solid oxide film; and

providing an air electrode on a surface of the solid oxide film formed on the fuel electrode.

According to the seventh aspect of the present invention, a method for manufacturing a solid oxide film comprises the following steps:

45 preparing a powder of compound containing at least one metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc;

preparing a solid oxide raw material;

supplying the compound and the solid oxide raw material to a spray gun via individually arranged powder supply devices;

50 melting the compound and the raw material in the spray gun;

spraying the melted compound and raw material on a substrate to form a sprayed solid oxide film thereon;

subjecting the thus formed sprayed solid oxide film to a heat treatment in order to improve airtightness of the solid oxide film formed on the substrate.

55 According to the eighth aspect of the present invention, a method for manufacturing a solid oxide fuel cell comprises the following steps:

preparing a powder of compound containing at least one metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc;

preparing a solid oxide raw material;  
 supplying the compound and the solid oxide raw material to a spray gun via individually arranged powder supply devices;  
 melting the compound and the material in the spraying gun;  
 5 spraying the melted compound and raw material on an air electrode to form a sprayed solid oxide film on the air electrode;  
 subjecting the solid oxide film formed on the air electrode to a heat treatment in order to improve airtightness of the solid oxide film; and  
 providing a fuel electrode on the solid oxide film formed on the air electrode.

10 According to the ninth aspect of the present invention, a method for manufacturing a solid oxide fuel cell comprises the following steps:

preparing a powder of compound containing at least one metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc;

preparing a solid oxide raw material;

15 supplying the compound and the solid oxide material to a spray gun via individually arranged powder supply devices;

melting the compound and the raw material in the spray gun;

spraying the melted compound and raw material on a fuel electrode to form a sprayed solid oxide film on the fuel electrode;

20 subjecting the solid oxide film formed on the fuel electrode to a heat treatment in order to improve airtightness of the solid oxide film; and

providing an air electrode on the solid oxide film formed on the air electrode.

It should be noted that the meaning of "spraying on a substrate" includes the case of spraying the material on a surface of the substrate and the case of spraying the solid oxide material on a surface of other  
 25 film, such as air electrode film and a fuel electrode film, formed on the surface of substrate; further the meaning of "spraying the solid oxide material on an air electrode (on a fuel electrode)" includes the case of spraying the solid oxide material on the surface of the air electrode film (fuel electrode film) formed on a surface of the porous substrate and the case of spraying the solid oxide material on a surface of an air electrode substrate made by an air electrode material (on a surface of a fuel electrode substrate made by a  
 30 fuel electrode material), respectively.

According to the present invention, since the sprayed solid oxide film is subjected to the heat treatment, the airtightness of the solid oxide film is improved. Therefore, there is no fine crack or fine defect, which are peculiarly caused in the process of the plasma spraying, and the structure of the solid oxide film is densified in an even manner. Further, since a solution of a compound containing at least one kind of metal  
 35 selected from the group of manganese, iron, cobalt, nickel, copper and zinc is impregnated into the sprayed solid oxide film, when subjecting the solid oxide film to a heat treatment, the densification of the structure of the sprayed solid oxide film is elevated, the required heat treatment temperature becomes low and the required heat treatment time becomes short. It should be noted that the same effects can be obtained in the case that an oxide of at least one kind of metal selected from the group of manganese, iron, cobalt, nickel,  
 40 copper and zinc is preliminarily included in the raw material for spraying and then the material is sprayed on the substrate and subjected to the heat treatment.

Further, it may be possible to arrange such that the compound powder containing at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc and a solid oxide material is supplied to the spray gun via individually arranged powder supply means and then the powder and the  
 45 material are melted in the spray gun. In this case, the above-mentioned metal is distributed in the sprayed solid oxide film as a whole in an even manner; and thus the densification of the structure of the sprayed solid oxide film is elevated much more when the sprayed solid film is subjected to the heat treatment.

As described in the above, according to the invention, it is possible to obtain the solid oxide film having the same airtightness and the same electric conductivity as the conventional solid oxide film, which is  
 50 manufactured by electrochemical vapor deposition, etc., by applying very easy techniques, such as spraying, impregnation and heat treatment. Therefore, the apparatus for manufacturing the solid oxide film can be made compact in size, and cheap in cost therefor, and further, the film is grown at a high speed and large size solid oxide film having a high airtightness can be obtained easily.

Thus, the solid oxide film manufactured by the method of the invention can be suitably used as a solid  
 55 oxide film for use as an oxygen sensor and a device for measuring oxygen concentration. Further, since the solid oxide film manufactured by the method of the invention has high airtightness, it can be used as a non-oxidizable film for coating a metal member.

Furthermore, since a thin solid oxide film having high airtightness and a high electric conductivity can

be obtained according to the invention, when use is made of a solid oxide film of a solid oxide fuel cell, the internal resistance of the cell becomes small and the power thereof becomes high.

Furthermore, in comparison the method of the invention with the conventional method, i.e. electrochemical vapor deposition, for manufacturing solid oxide film, the technique of the present invention is much easier than the conventional method, and only the simple devices such as a general spraying device and an electric furnace for the heat treatment are required to grow the film; thus the manufacturing cost for the film becomes lower.

Moreover, by the conventional method, i.e. electrochemical vapor deposition, manufacturing a comparatively small-sized cylindrical solid oxide fuel cell is possible, but, it is difficult to manufacture a plate-like solid oxide fuel cell. In contrast to this, the present invention can be applied for manufacturing both the cylindrical solid oxide fuel cell and the plate-like solid oxide fuel cell. Additionally, the present invention can easily be applied for manufacturing not only the prolonged cylindrical cell and the plate-like cell having a large area but also a collecting cell having a complex shape.

A mixture or a solid solution consisting of an alkali-earth metal or rare-earth metal and a ceric oxide or zirconium oxide is preferably used as the solid oxide material. In case that at least one kind of metal selected from a group of manganese, iron, cobalt, nickel copper and zinc is contained in the solid oxide material for spraying, a compound (for example, oxide) of the above mentioned metal or metals is added to a powder of said mixture or said solid solution, and then the compound and the powder are mixed to obtain a mixed powder; and the thus obtained mixed powder is preliminarily sintered to solute the metal component or components into the material for spraying. The metal component or components serve to make the required heat treatment temperature low and the required heat treatment time short.

Then, the solid oxide material for spraying obtained in such a manner is sprayed on a substrate to form a sprayed solid oxide film on the substrate. Spraying is conducted with the aid of plasma spraying method. It should be noted that the plasma spraying under a lower pressure is much more effective than the plasma spraying under a normal pressure. But, even if the plasma spraying is conducted under the normal pressure, the solid oxide film would have enough airtightness by the heat treatment conducted thereafter.

As the other method for manufacturing the solid oxide film, spraying the solid oxide material on a substrate; impregnating a solution of compound containing at least one kind of said metals into the film; drying the film; and then conducting a heat treatment with the film. In this case, acetates, nitrates, sulfates, and salts of organic acids of said metals are preferably used as the compound. Further, it may be possible to impregnate the solution not only the solid oxide film but also the film and substrate. Furthermore, in order to impregnate the solution at least into the film, it is preferred to immerse the sprayed solid oxide film, and the film and substrate as demanded, into the solution.

In the case that a compound powder containing at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc and a solid oxide material is melted in a spray gun, oxide, carbonate or hydroxide of the metal or metals is preferably used as the compound. In this case, the compound powder and the solid oxide material are supplied to the spray gun via separately arranged powder supply devices. Therefore, it may be possible to make a gradient in a composition of the sprayed solid oxide film by varying the supplied amounts of the compound powder and the solid oxide material as time is passed and as occasion demands.

In the case of spraying a solid oxide material mainly consisting of zirconium oxide on the surface of an air electrode, an insulating layer consisting of  $\text{La}_2\text{Zr}_2\text{O}_7$ , etc. may be produced between the solid oxide film and the air electrode at the step of the heat treatment conducted thereafter. However, by the existence of manganese or cobalt in the sprayed solid oxide film in accordance with the invention, such insulating layer would not be produced.

Fig. 1 is a schematic partial front view showing an example of plane type SOFC, and Figs. 2 and 3 are partial perspective views depicting an example of cylindrical type SOFC.

In the example shown in Fig. 1, a solid oxide film 2 is formed on a surface of a plate-like air electrode substrate 1, which is made by air electrode material; and on a surface of the solid oxide film is arranged a fuel electrode 3. It may be possible to arranged such that the solid oxide film is formed on a surface of a plate-like fuel electrode substrate, which is made by a fuel electrode material, and further arrange an air electrode on the surface of the solid oxide film.

In the example depicted in Fig. 2, a solid oxide film 12 is provided on a surface of a cylindrical air electrode substrate 11 made by an air electrode material; and on a surface of the solid oxide film 12 is arranged a fuel electrode film 13. There is arranged an interconnector 6 on the air electrode substrate 11 in a right upper region in Fig. 2; additionally a connecting terminal 7 is arranged on the interconnector 6. A plurality of cylindrical SOFCs are connected to each other in series by connecting the air electrode substrate 11 of the SOFC and the fuel electrode film 13 of contiguously arranged SOFC via the

interconnector 6 and the connecting terminal 7; and these cylindrical SOFCs are connected to each other in parallel by connecting the fuel electrode films 13 to each other by means of a metal felt such as Ni felt. Contrary to the configuration, it may be possible to arrange the solid oxide film on a cylindrical fuel electrode substrate made by the fuel electrode material and to arrange the air electrode film on the surface of the solid oxide film.

In the SOFC illustrated in Fig. 3, an air electrode film 21 is formed around an outer circumference of a cylindrical substrate 4 made of a porous ceramic; and a solid oxide film 12 and fuel electrode film 13 are arranged around the outer circumference of the air electrode film 21 in this order. The other construction is the same as the SOFC depicted in Fig. 2, and the explanation therefor is omitted. It may be also possible to exchange the arrangement of the air electrode film 21 and the fuel electrode film 13.

The air electrode may be produced by a doped or non-doped oxide such as  $\text{LaMnO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{LaNiO}_3$ ,  $\text{LaCoO}_3$  and  $\text{LaCrO}_3$ ; but strontium-doped or calcium-doped  $\text{LaMnO}_3$  is preferred. These doped or non-doped  $\text{LaMnO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{LaNiO}_3$ ,  $\text{LaCoO}_3$ ,  $\text{LaCrO}_3$  are not limited to an oxide having a definite composition but an oxide having a non-definite composition such as La lacking composition and Ca lacking composition can be used. The oxide having a non-definite composition effects to limit the production of  $\text{La}_2\text{Zr}_2\text{O}_7$ . The fuel electrode made of Nickel-Zirconia cermet or Cobalt-Zirconia cermet is preferably used. A gas including a fuel such as hydrogen, reformed hydrogen, carbon monoxide and hydrocarbon is used as a fuel gas and a gas including an oxidizing agent such as oxygen, hydrogen peroxide, etc. is used as an oxidized gas.

Fig. 1 is a partial front view showing a plate-like SOFC.

Fig. 2 is a partial perspective view illustrating a cylindrical SOFC; and

Fig. 3 is a partial perspective view indicating another cylindrical SOFC.

#### Embodiment 1

Eight mol. %  $\text{Y}_2\text{O}_3$  stabilized zirconia powder were molded under a molding pressure of 200 kg/cm<sup>2</sup> to obtain circular plates having a diameter of 70 mm and thickness of 3 mm. The plate was sintered for five hours at a temperature of 1450°C and then processed to obtain a circular plate-like substrates having diameters of 50 mm, thicknesses of 1 mm and porosities of 23%. Eight mol. %  $\text{Y}_2\text{O}_3$  stabilized zirconia (8YSZ) powder were prepared as the solid oxide material; and the powder was sprayed on the substrates with the aid of the plasma spraying to form films of 8YSZ thereon with thicknesses of 500  $\mu\text{m}$ . Then the substrates were ground off by buffing to obtain only the sprayed solid oxide films. Twenty grams of manganese acetate were soluted in eighty grams of water; and the sprayed solid oxide film was immersed therein; then the manganese acetate was impregnated into the solid oxide films by degassing in a vacuum. Then, the solid oxide films were dried at a temperature of 100°C. The impregnation and drying were repeated to obtain sprayed solid oxide films which are different in the number of time of impregnation. The heat treatment was conducted on the thus obtained Mn impregnated sprayed solid oxide films and non-impregnated sprayed solid oxide films except the comparative example, respectively, at a temperature of 1300–1450°C for three hours. A permeation amount of  $\text{N}_2$  gas was measured after conducting the heat treatment concerning each the sprayed solid oxide film. The measurement result is shown in Table 1.

Table 1

	Thickness of sprayed film ( $\mu\text{m}$ )	Number of times of impregnation	Heat treatment temperature ( $^{\circ}\text{C}$ )	Permeation amount of $\text{N}_2$ ( $\text{cc} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ )
Comparative sample	500	non	non	3
Reference sample	500	non	1450	0.09
Present invention	500	1	1450	0.001
Present invention	500	2	1350	0.02
Present invention	500	10	1300	0.1
Present invention	500	2	1300	0.4

In the same manner, but with the solution of compound for impregnation was altered by iron acetate, nickel nitrate, cobalt acetate, copper sulfate or zinc acetate, the experiment was conducted. Each solid

oxide film was subjected to a heat treatment after the impregnation was conducted two times. Then the permeation amount of N<sub>2</sub> gas through each film was measured in the same manner. The experimental results are shown in Table 2.

Table 2

	Thickness of sprayed film (μm)	Impregnation liquid	Heat treatment temperature (°C)	Permeation amount of N <sub>2</sub> (cc·min <sup>-1</sup> ·cm <sup>-2</sup> )
Present invention	500	iron acetate	1400	0.003
Present invention	500	nickel nitrate	1400	0.009
Present invention	500	cobalt acetate	1400	0.006
Present invention	500	copper sulfate	1400	0.003
Present invention	500	zinc acetate	1400	0.003

## Embodiment 2

The following is an embodiment of the method for manufacturing a solid oxide fuel cell.

Lanthanum manganite powder was molded under a molding pressure of 200 kg/cm<sup>2</sup> to obtain bodies each having a diameter of 50 mm and thickness of 3 mm then the bodies were sintered at a temperature of 1450 °C for five hours and the sintered bodies were processed to obtain air electrode substrates each having a diameter of 30 mm, thickness of 1 mm and porosity of 25%. Eight mol % Y<sub>2</sub>O<sub>3</sub> stabilized zirconia (8YSZ) powder were prepared; and the powder was sprayed on the air electrode substrates with the aid of plasma spraying to form an 8YSZ layer having a thickness of 200 μm on each substrate. Then the laminated bodies were immersed into a solution of 20g of manganese acetate and 80g of water at the normal temperature; and then the bodies were degassed in the vacuum in order to impregnate the bodies with the manganese acetate. Thereafter, the laminated bodies were dried at a temperature of 100 °C. The impregnation and drying processes were repeated to obtain several kinds of the laminated bodies, to which the impregnation and drying were applied in different number of times. The thus obtained laminated bodies containing manganese and layered bodies containing no manganese were subjected to a heat treatment at a predetermined temperature for three hours. It should be noted that no heat treatment was conducted on a comparative sample. Further, nickel zirconia paste is applied on the surface of the solid oxide films formed on the air electrode substrates with the aid of screen printing; then the bodies were sintered at a temperature of 1200 °C for three hours to form a fuel electrode on each solid oxide film. On the air electrodes of the thus obtained unit solid oxide fuel cells, was fed oxygen gas and on the fuel electrodes thereof, was fed H<sub>2</sub> + H<sub>2</sub>O to measure open circuit voltages OCV of the unit cells. Further, the resistances of the unit cells were measured by a cole-cole-plot. Furthermore, an existence of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> layer was recognized by SEM (reflected image of an electron) of a polished cross-section of the laminated body. The measurement result is shown in Table 3.

Table 3

	Thickness of sprayed film ( $\mu\text{m}$ )	Number of times of immersion	Heat treatment temperature ( $^{\circ}\text{C}$ )	Open circuit voltage OCV	Resistant ( $\Omega \cdot \text{cm}^2$ )	$\text{La}_2\text{Zr}_2\text{O}_7$ layer
Comparative sample	200	non	non	0.89	1.0	non
Reference sample	100	non	1400	1.00	0.9	exist
Reference sample	100	non	1500	1.11	1.2	exist
Present invention	200	1	1500	1.11	0.4	little
Present invention	200	1	1400	1.11	0.3	non
Present invention	200	10	1300	1.11	0.2	non
Present invention	50	1	1300	1.05	0.08	non
Present invention	100	1	1300	1.08	0.1	non
Present invention	200	1	1300	1.09	0.2	non

As clear from the embodiments 1 and 2, it is possible to airtight the sprayed solid oxide layer, according to the present invention. Additionally, in case the solid oxide film is applied to the solid oxide fuel cell, the open circuit voltage of the cell is improved by a combination of the impregnation of manganese and the heat treatment; and the resistance of the cell can be made remarkably small because an  $\text{La}_2\text{ZrO}_3$  having an insulating property is not generated or generated slightly when subjecting the cell to the heat treatment due to the impregnation of manganese. In comparison the solid oxide fuel cell according to the present invention with the reference solid oxide fuel cell, when the cell is manufactured under the condition that the heat treatment temperature is considerably low, the open circuit voltage of the cell becomes close to the theoretical value 1.11 V, because of the impregnation of manganese.

### Embodiment 3

Eight mol %  $\text{Y}_2\text{O}_3$  stabilized zirconia powder were molded under a molding pressure of 200 kg/cm<sup>2</sup> to obtain circular plate-like molding bodies each having diameter of 50 mm and thickness of 3 mm; the bodies were sintered at a temperature of 1450  $^{\circ}\text{C}$  for five hours; and then the sintered bodies were processed to obtain substrates for spraying each having a diameter of 30 mm, a thickness of 1 mm and a porosity of 25%. Eight mol %  $\text{Y}_2\text{O}_3$  stabilized zirconia (8YSZ) powder were prepared as a solid oxide raw material; and 0.5 parts by weight, 1 parts by weight, 5 parts by weight or 10 parts by weight of the metal oxides shown in Table 4 were added with respect to 100 parts by weight of the 8YSZ powder: then into the thus obtained metal oxide mixed powders were added 1 kg of water and then mixed with the aid of an attritor to obtain slurries. The slurries were grained into fine grains having mean diameter of 30  $\mu\text{m}$ , by a spray dryer; then the fine grains were preliminarily sintered at a temperature of 1200  $^{\circ}\text{C}$  for three hours; and the sintered grains were put through a sieve of 44  $\mu\text{m}$  mesh to obtain raw material powders for spraying. The thus obtained raw material powders for spraying were sprayed on the surfaces of said substrates by plasma spraying to laminate the 8YSZ layer of 200  $\mu\text{m}$  or 500  $\mu\text{m}$ . Thereafter, the substrates were ground off to take out only the sprayed solid oxide films. The thus taken out films were subjected to a heat treatment at temperatures shown in the Table 4 for five hours, respectively; and then  $\text{N}_2$  gas transmitting coefficients were measured concerning each example. The measurement result is shown in Table 4.

Table 4

	Thickness of sprayed film ( $\mu\text{m}$ )	Additive	Adding amount	Heat treatment temperature ( $^{\circ}\text{C}$ )	Permeation coefficient of $\text{N}_2$ ( $\text{cm}^4 \cdot \text{g}^{-1} \cdot \text{S}^{-1}$ )
Comparative sample	500	non	non	non	$5 \times 10^{-5}$
Reference sample	500	non	non	1450	$8 \times 10^{-6}$
Reference sample	500	$\text{MnO}_2$	0.5	1450	$7 \times 10^{-6}$
Present invention	500	$\text{MnO}_2$	1	1450	$3 \times 10^{-9}$
Present invention	500	$\text{Fe}_2\text{O}_3$	5	1350	$4 \times 10^{-8}$
Present invention	500	$\text{Fe}_2\text{O}_3$	5	1300	$7 \times 10^{-7}$
Present invention	200	$\text{NiO}$	10	1350	$7 \times 10^{-8}$

#### Embodiment 4

The following is another embodiment of a method for manufacturing solid oxide fuel cell.

Lanthanum manganite powder was molded under a molding pressure of  $200 \text{ kg/cm}^2$  to obtain circular platelike molded bodies having a diameter of 50 mm and thickness of 3 mm; the molded bodies were sintered at a temperature of  $1450^{\circ}\text{C}$  for five hours; and then the sintered bodies were processed to obtain air electrode substrates having diameters of 30 mm, thicknesses of 1 mm and porosities of 25%. Eight mol %  $\text{Y}_2\text{O}_3$  stabilized zirconia (8YSZ) powder (electrofused zirconia) were prepared as a material for spraying; and a predetermined amount of metal oxides shown in the following Table 5 were added into the material, respectively; and each material and each of the metal oxide were mixed with each other in a pot mill with organic gravel for four hours; the mixed materials were sintered at a temperature of  $1300^{\circ}\text{C}$  for five hours and then were put through a sieve of  $149 \mu\text{m}$  mesh to obtain a plurality of kinds of material powders for spraying. The thus obtained material powders for spraying were sprayed on the surfaces of the air electrode substrates, respectively, to form a laminate layer of 8YSZ having a predetermined thickness on each substrate. The thus obtained sprayed solid oxide films were subjected to heat treatments at temperatures shown in the Table 5. Further, a nickel zirconia paste was applied on the surfaces of the solid oxide films by means of screen printing; and then the films were sintered at a temperature of  $1200^{\circ}\text{C}$  for three hours to form fuel electrode films on the solid oxide film. On the air electrodes of the thus obtained single solid oxide fuel cells, was fed an oxygen gas and on the fuel electrodes thereof, was fed  $\text{H}_2 + \text{H}_2\text{O}$  to measure an open circuit voltage OCV under a temperature of  $1000^{\circ}\text{C}$ . Further, the resistance of the unit cells were measured by a cole-cole-plot. The measurement result was shown in Table 5. The amount of additive is parts by weight per hundred of 8YSZ.

Table 5

	Thickness of sprayed film ( $\mu\text{m}$ )	Additive	Adding amount	Heat treatment temperature ( $^{\circ}\text{C}$ )	Open circuit voltage OCV	Resistance ( $\Omega \cdot \text{cm}^2$ )
Comparative sample	200	non	non	non	0.89	1.2
Reference sample	100	non	non	1550	1.00	0.9
Reference sample	100	non	non	1600	1.11	1.2
Present invention	200	$\text{MnO}_2$	1	1500	1.11	0.4
Present invention	200	$\text{MnO}_2$	1	1400	1.11	0.5
Present invention	200	$\text{CoO}$	10	1300	1.08	0.3
Present invention	50	$\text{CuO}$	1	1300	1.05	0.1
Present invention	100	$\text{ZnO}$	1	1300	1.08	0.2
Present invention	200	$\text{ZnO}$	1	1300	1.09	0.3
Comparative sample	200	$\text{MnO}_2$	12	non	0.85	0.9
Reference sample	100	$\text{CuO}$	11	1400	0.88	0.7

As apparent from the above explained embodiments 3 and 4, by adding a specific metal oxide into the material for spraying and subjecting the sprayed solid oxide fuel films to a heat treatment, the open circuit voltage of the solid oxide fuel cell becomes the theoretical value of 1.11 V or becomes close thereto, and the resistance of the cell becomes very small, in comparison with the solid oxide fuel cells of the comparative sample, which were manufactured without being subjected to the heat treatment. Further, comparing the solid oxide fuel cells manufactured by the method according to the present invention with the reference solid oxide fuel cells, the resistances of the cells according to the invention is lower than the reference samples and the voltages at the open circuits are higher than those of the reference samples regardless of the lower heat treatment temperature. The reason why the resistance of the cells of the present invention becomes lower by adding the specific metal oxides is that the  $\text{La}_2\text{Zr}_2\text{O}_7$  is not produced or only a little  $\text{La}_2\text{Zr}_2\text{O}_7$  is produced during the cells are subjected to the heat treatment. Further, when adding the amount of specific metal oxide exceeds over 10 parts by weight, the voltage at the open circuits decreases and the resistance of the unit cell becomes high. On the contrary, when the added amount of specific metal oxide is less than 1 part by weight, the sprayed solid oxide film is not densified so much, and then the permeation coefficient of  $\text{N}_2$  does not become small, and the effect to reduce the generation of the insulating material of  $\text{La}_2\text{Zr}_2\text{O}_7$  can not be obtained sufficiently.

#### Embodiment 5

Eight mol %  $\text{Y}_2\text{O}_3$  stabilized zirconia powder were molded at a molding pressure of 200  $\text{kg/cm}^2$  to obtain molded circular plate-like bodies having diameters of 50 mm and thicknesses of 3 mm; the molded bodies were sintered at a temperature of 1450  $^{\circ}\text{C}$  for five hours and then processed to obtain circular substrates for spraying having diameters of 30 mm, thicknesses of 1 mm and porosities of 25%. Eight mol %  $\text{Y}_2\text{O}_3$  stabilized zirconia powder and metal oxides shown in Table 6 were prepared as a material for spraying. The 8YSZ powder and each metal oxide powder were fed to a spray gun via the separately arranged powder supply devices, respectively, and melted in the spray gun. The melted materials were sprayed on the surfaces of the substrates for spraying with the aid of plasma spraying to get a plurality of kinds of solid oxide films. The thicknesses of the sprayed layers were 200  $\mu\text{m}$  or 500  $\mu\text{m}$ . Then, the substrates for spraying were ground off to take out only sprayed solid oxide films. The thus obtained solid oxide films were subjected to heat treatments at the temperatures shown in Table 6 for five hours and then the permeation coefficients of  $\text{N}_2$  gas concerning the respective films were measured. The measurement results are shown in Table 6. It should be noted that in the item of "adding amount" in Table 6 the supply amount of each metal oxide powder is indicated by using a unit of part by weight with respect to the supply amount of 100 parts by weight of 8YSZ powder.

Table 6

	Thickness of sprayed film ( $\mu\text{m}$ )	Metal oxide	Adding amount	Heat treatment temperature ( $^{\circ}\text{C}$ )	Permeation coefficient of $\text{N}_2$ ( $\text{cm}^4 \cdot \text{g}^{-1} \cdot \text{S}^{-1}$ )
Comparative sample	500	non	non	non	$5 \times 10^{-5}$
Reference sample	500	non	non	1450	$8 \times 10^{-6}$
Present sample	500	$\text{MnO}_2$	0.5	1450	$1 \times 10^{-6}$
Present invention	500	$\text{MnO}_2$	1	1450	$2 \times 10^{-9}$
Present invention	500	$\text{Fe}_2\text{O}_3$	5	1350	$1 \times 10^{-8}$
Present invention	500	$\text{Fe}_2\text{O}_3$	5	1300	$8 \times 10^{-7}$
Present invention	200	$\text{NiO}$	10	1350	$9 \times 10^{-8}$

#### Embodiment 6

The following is another embodiment for manufacturing a solid oxide fuel cell in which the solid oxide film formed by the method according to the fifth embodiment explained in the above.

Lanthanum manganite powder was molded at a molding pressure of  $200 \text{ kg/cm}^2$  to obtain circular plate-like molded bodies having diameters of 50 mm and thicknesses of 3 mm. These bodies were sintered at a temperature of  $1450^{\circ}\text{C}$  for five hours and then processed to obtain air electrode substrates having diameters of 30 mm, thicknesses of 1 mm and porosities of 25%, respectively. Eight mol %  $\text{Y}_2\text{O}_3$  stabilized zirconia (8YSZ) powder (electrofused zirconia) and metal oxide powders shown in Table 7 were prepared as a material for spraying. These 8YSZ powder and each metal oxide powder were fed to a spray gun via the separately arranged powder supply devices and melted in the spray gun to get a plurality of kinds of melted material. The melted materials were sprayed on the surfaces of the air electrode substrates by means of plasma spraying to obtain sprayed films having thicknesses shown in Table 7 on the substrates. Then these sprayed solid oxide films were subjected to heat treatments at temperatures shown in Table 7. Further, a nickel zirconia paste was applied on the respective solid oxide films by means of screen printing, and the paste applied films with nickel zirconia paste were sintered at a temperature of  $1200^{\circ}\text{C}$  for three hours to obtain fuel electrode films on the solid oxide film. Oxygen gas was supplied onto the air electrodes and  $\text{H}_2 + \text{H}_2\text{O}$  onto the fuel electrodes; and then voltages at the open circuit OCV of the respective cells were measured at a temperature of  $1000^{\circ}\text{C}$ . Further, resistances of the respective cells were measured by a cole cole plot. These measurement result are shown in Table 7. It should be noted, in an item of "adding amount" in Table 7, the supply amount of metal oxide is indicated by using a unit part by weight with respect to when the supply amount of 100 parts by weight of 8YSZ powder.

Table 7

	Thickness of sprayed film ( $\mu\text{m}$ )	Metal oxide	Adding amount	Heat treatment temperature ( $^{\circ}\text{C}$ )	Open circuit voltage OCV	Resistance ( $\Omega \cdot \text{cm}^2$ )
Comparative sample	200	non	non	non	0.89	1.2
Reference sample	100	non	non	1550	1.00	0.9
Reference sample	100	non	non	1600	1.11	1.2
Present invention	200	$\text{MnO}_2$	1	1500	1.11	0.3
Present invention	200	$\text{MnO}_2$	1	1400	1.11	0.4
Present invention	200	$\text{CoO}$	10	1300	1.08	0.4
Present invention	50	$\text{CuO}$	1	1300	1.04	0.2
Present invention	100	$\text{ZnO}$	1	1300	1.09	0.2
Present invention	200	$\text{ZnO}$	1	1300	1.10	0.4
Comparative sample	200	$\text{MnO}_2$	12	non	0.87	0.9
Present sample	100	$\text{CuO}$	11	1400	1.00	0.6

As apparent from the above embodiments, when the solid oxide material and metal oxide powder were fed into the spray gun via the separately arranged powder supply devices and then the melted materials were subjected to the heat treatment, the same effect as those of the first to fourth embodiments can be obtained.

As explained in detail in the above, according to the invention, it is possible to solve the drawbacks of fine cracks or defects, which are generated in the solid oxide film manufactured with the aid of plasma spraying, and possible to obtain a solid oxide film having a high density and even structure. Further, by impregnating a specified metal into the sprayed solid oxide film by the method mentioned in the above, the structure of the film is elevated to be densified during when the sprayed solid oxide film is subjected to a heat treatment. Therefore, it is possible to make the required heat treatment temperature low and the required heat treatment time short. In such manner, according to the invention, the solid oxide film having the same airtightness and the same electric conductivity as those of the conventional solid oxide film having a high airtightness manufactured by an EVD method, etc. can be obtained with the aid of a very easy techniques such as spraying, impregnation and heat treatment. Therefore, the equipment for manufacturing the solid oxide film can be made compact, the cost therefore kept low, the speed for film growth high, and highly densified solid oxide film having a large area can be obtained easily.

#### Claims

1. A method for manufacturing a solid oxide film comprising the following steps:  
preparing a solid oxide material;  
spraying said solid oxide material on a substrate to form a sprayed solid oxide film;  
impregnating a solution of a compound containing at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc into said sprayed solid oxide film; and  
subjecting the solid oxide film to a heat treatment in order to improve an airtightness of the solid oxide film formed on the substrate.
2. A method for manufacturing a solid oxide film according to Claim 1, wherein:  
said solid oxide material is a mixture or a solid solution consisting of alkali-earth metal or rare-earth metal and cerium oxide or zirconium oxide.
3. A method for manufacturing a solid oxide fuel cell comprising the following steps of:  
preparing a solid oxide material;  
spraying said solid oxide material on an air electrode to form a sprayed solid oxide film on the air electrode;

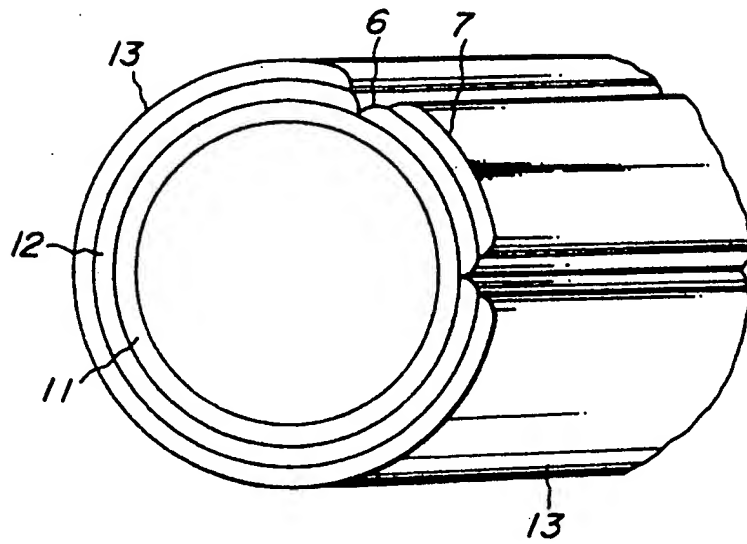
- impregnating a solution of a compound containing at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc into said solid oxide film formed on the air electrode;
- subjecting the sprayed solid oxide film to a heat treatment in order to improve an airtightness of the solid oxide film; and
- providing a fuel electrode film on a surface of the solid oxide film formed on the air electrode.
4. A method for manufacturing a solid oxide fuel cell comprising the following steps of:
- preparing a solid oxide material;
- spraying said solid oxide material on a fuel electrode to form a sprayed solid oxide film on the fuel electrode;
- impregnating a solution of a compound containing at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc into said solid oxide film formed on the fuel electrode;
- subjecting the sprayed solid oxide film to a heat treatment in order to improve an airtightness of the solid oxide film formed on the fuel electrode; and
- providing an air electrode film on a surface of the solid oxide film formed on the fuel electrode.
5. A method for manufacturing a solid oxide film comprising the following steps:
- preparing a solid oxide material for spraying containing 1~10 parts by weight in total of an oxide of at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc with respect to 100 parts by weight of solid oxide raw material;
- spraying the thus prepared solid oxide material on a substrate to form a solid oxide film on the substrate;
- subjecting the thus formed solid oxide film to a heat treatment in order to improve an airtightness of the solid oxide film formed on the substrate.
6. A method for manufacturing a solid oxide fuel cell comprising the following steps:
- preparing a solid oxide material for spraying containing 1~10 parts by weight in total of an oxide of at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc with respect to 100 parts by weight of solid oxide raw material;
- spraying the thus prepared solid oxide material on an air electrode to form a solid oxide film on the air electrode;
- subjecting the solid oxide film formed on the air electrode to a heat treatment in order to improve an airtightness of the solid oxide film; and
- providing a fuel electrode on a surface of the solid oxide film formed on the air electrode.
7. A method for manufacturing a solid oxide fuel cell comprising the following steps:
- preparing a solid oxide material for spraying containing 1~10 parts by weight in total of an oxide of at least one kind of metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc with respect to 100 parts by weight of solid oxide raw material;
- spraying the thus prepared solid oxide material on a fuel electrode to form a solid oxide film on the fuel electrode;
- subjecting the solid oxide film formed on the fuel electrode to a heat treatment in order to improve an airtightness of the solid oxide film; and
- providing an air electrode on a surface of the solid oxide film formed on the fuel electrode.
8. A method for manufacturing a solid oxide film comprising the following steps:
- preparing a powder of compound containing at least one metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc;
- preparing a solid oxide raw material;
- supplying the compound and the solid oxide raw material to a spray gun via individually arranged powder supply devices;
- melting the compound and the raw material in the spray gun;
- spraying the melted compound and raw material on a substrate to form a sprayed solid oxide film thereon;
- subjecting the thus formed sprayed solid oxide film to a heat treatment in order to improve an airtightness of the solid oxide film formed on the substrate.

9. A method for manufacturing a solid oxide film according to Claim 8, wherein:  
said compound powder is metal oxide, **carbonate** or hydroxide of one of said metals.
10. A method for manufacturing a solid oxide fuel cell comprising the following steps:  
5     preparing a powder of compound containing at least one metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc;  
       preparing a solid oxide raw material;  
       supplying the compound and the solid oxide raw material to a spray gun via individually arranged powder supply devices;  
10     melting the compound and the material in the spraying gun;  
       spraying the melted compound and raw material on an air electrode to form a sprayed solid oxide film on the air substrate;  
       subjecting the solid oxide film formed on the air electrode to a heat treatment in order to improve an airtightness of the solid oxide film; and  
15     providing a fuel electrode on the solid oxide film formed on the air electrode.
11. A method for manufacturing a solid oxide fuel cell comprising the following steps:  
       preparing a powder of compound containing at least one metal selected from a group of manganese, iron, cobalt, nickel, copper and zinc;  
20     preparing a solid oxide raw material;  
       supplying the compound and the solid oxide material to a spray gun via individually arranged powder supply devices;  
       melting the compound and the raw material in the spray gun;  
       spraying the melted compound and raw material on a fuel electrode to form a sprayed solid oxide  
25     film on the fuel substrate;  
       subjecting the solid oxide film formed on the fuel electrode to a heat treatment in order to improve the airtightness of the solid oxide film; and  
       providing an air electrode on the solid oxide film formed on the fuel electrode.
- 30   12. A method for manufacturing a solid oxide fuel cell according to one of Claims of 3, 4, 6, 7, 10 or 11, wherein:  
       said air electrode is formed by a doped or non-doped  $\text{LaMnO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{LaNiO}_3$ ,  $\text{LaCoO}_3$  or  $\text{LaCrO}_3$ .
- 35   13. A method for manufacturing a solid oxide fuel cell according to Claim 12, wherein:  
       said doped or non-doped  $\text{LaMnO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{LaNiO}_3$ ,  $\text{LaCoO}_3$  or  $\text{LaCrO}_3$  has a **stoichiometric composition**.
- 40   14. A method for manufacturing a solid oxide fuel cell according to Claim 12, wherein:  
       said doped or non-doped  $\text{LaMnO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{LaNiO}_3$ ,  $\text{LaCoO}_3$  or  $\text{LaCrO}_3$  has a **non-stoichiometric composition**.

**FIG. 1**



**FIG. 2**



**FIG. 3**

